# Comment on "Nature and entropy content of the ordering transitions in $RCo_2$"

M. Forker,* S. Müller, and P. de la Presa†
*Helmholtz-Institut für Strahlen- und Kernphysik der Universität Bonn, Nussallee 14-16, D-53115 Bonn, Germany*

A. F. Pasquevich
*Departamento de Fisica, Facultad de Ciencias Exactas, Universidad de La Plata. C.C. No. 67, 1900 La Plata, Argentina*
(Received 23 June 2006; revised manuscript received 30 August 2006; published 9 May 2007)

In their analysis of our perturbed angular correlation (PAC) study of the magnetic phase transitions of $RCo_2$ [Phys. Rev. B **68**, 014409 (2003)], Herrero-Albillos *et al.* [Phys. Rev. B **73**, 134410 (2006)] come to the conclusion that it is very difficult for PAC spectroscopy to distinguish a first-order from a second-order phase transition. The statement is incorrect and does not resolve the conflict between the conclusion drawn from the PAC data and the differential scanning calorimetry data of Herrero-Albillos *et al.* on the order of the magnetic phase transitions of $PrCo_2$ and $NdCo_2$. In this Comment we show that measurements of hyperfine interactions by PAC and other microscopic techniques are a very powerful tool for the investigation of phase transitions which may provide details on the transition not accessible to macroscopic methods. We explain why the PAC data leave no alternative to the conclusion that the spontaneous magnetization of $PrCo_2$ and $NdCo_2$ undergoes a discontinuous, first-order phase transition at $T_C$.

DOI: 10.1103/PhysRevB.75.187401 PACS number(s): 75.30.Sg, 65.40.Gr, 71.20.Lp

In a recent differential scanning calorimetry (DSC) study of the magnetic phase transitions of the rare earth ($R$) Laves phases $RCo_2$ Herrero-Albillos *et al.*[1,2] report that the magnetic phase transitions of the light $R$ compounds $PrCo_2$ and $NdCo_2$ are second-order transitions (SOT). This conclusion is in conflict with the results of a perturbed angular correlation (PAC) investigation[3] of $RCo_2$ according to which the magnetization of $PrCo_2$ and $NdCo_2$ undergoes a first-order transition (FOT). As documented in Ref. 3, earlier studies of $PrCo_2$ and $NdCo_2$ have not been conclusive as to the order of the phase transition of these compounds.

In an attempt to resolve the conflict between the DSC and the PAC results at the expense of the hyperfine spectroscopic technique, Herrero-Albillos *et al.*[1] state: "The lack of a fine temperature scanning near $T_C$ together with the cited phase-coexistence makes it very difficult to use PAC spectra as a tool to discriminate between first- and second-order phase transitions. In contrast, DSC is the technique of choice when aiming at determine the nature of a transition, especially in those cases hard to discriminate."

This assessment creates an incorrect impression of the potential and precision of hyperfine interaction (HFI) techniques (PAC, Moessbauer, NMR, and others) for the investigation of phase transitions[4] and ignores the fundamental difference between macroscopic techniques which average over $mm^3$ samples and microscopic methods with nanometer spatial resolution. The statement asks for a correcting comment, primarily because of the special importance of the order of the phase transitions of $PrCo_2$ and $NdCo_2$ for the theory of the itinerant electron magnetism of $RCo_2$, (Refs. 5–8), but also to oppose the dissemination of mistaken ideas about the role hyperfine interactions can and cannot play in solid state research.

In the PAC experiment[3] the order of the phase transitions of $RCo_2$ was derived from the temperature dependence of the magnetic hyperfine interaction of the probe nucleus $^{111}Cd$ which resides on the cubic $R$ site.[9] The interaction of the magnetic dipole moment of the $I=5/2$, 245 keV state of $^{111}Cd$ with the magnetic hyperfine field acting at the probe site was determined by observing the time dependence of the anisotropy[10] of the 171–245 keV $\gamma$-$\gamma$ cascade of $^{111}Cd$ at different temperatures. Figure 1 illustrates the typical thermal evolution of the PAC spectra for a second-order ($GdCo_2$; $T_{C0}=392$ K) and a first-order transition ($PrCo_2$; $T_{C0}=39.9$ K) compound. For the sake of comparability, the temperatures are given in units of $T/T_{C0}$ where $T_{C0}$ is the most frequent order temperature of a $T_C$ distribution with a width of 1–2 K.[3] At the lowest temperature of 10 K, the PAC spectra of both compounds show a periodic modulation of the anisotropy with time which reflects the Larmor precession of the nuclear spins with magnetic frequency $\upsilon_M$

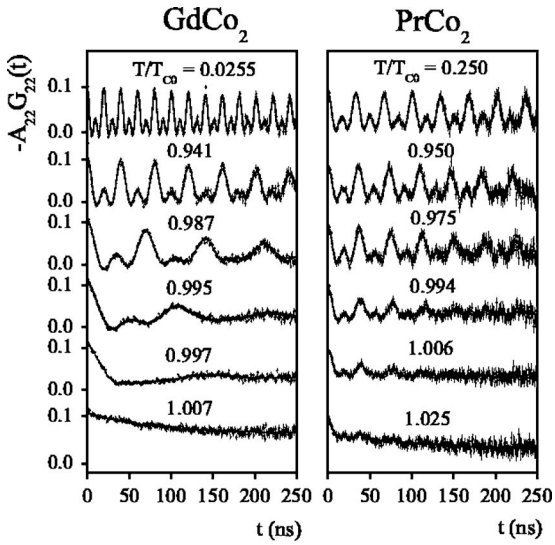


FIG. 1. PAC spectra of $^{111}Cd$ in $GdCo_2$ and $PrCo_2$ at different temperatures. These are given in units of $T/T_{C0}$ where $T_{C0}$ is the most frequent order temperature of a $T_C$ distribution with a width of 1–2 K.

 

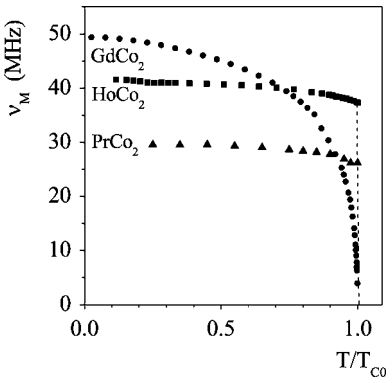


FIG. 2. The temperature dependence of the magnetic interaction frequency of $^{111}$Cd in $GdCo_2$, $HoCo_2$, and $PrCo_2$.

$=g\mu_N B_{hf}/h$ ($g$ denotes the nuclear $g$ factor, $B_{hf}$ the magnetic hyperfine field). With temperature increasing towards the phase transition, the Larmor frequency of $^{111}$Cd in $GdCo_2$ decreases continuously; at $T/T_{C0}=0.941$ the frequency has decreased by about a factor of 2 and at $T/T_{C0}=0.995$ by a factor of almost 6. It is easy to see that in contrast to $GdCo_2$, the period of the Larmor precession in $PrCo_2$ remains practically constant up to the Curie temperature. At $T/T_{C0}=0.994$ one finds $\nu_M(T)=0.88\ \nu_M(10\ \mathrm{K})$. The temperature dependencies of the Larmor frequency of $^{111}$Cd in $GdCo_2$ and $PrCo_2$ are compared in Fig. 2, which also shows the frequencies of a compound with an unquestioned FOT ($HoCo_2$). Details on the extraction of the frequencies from the PAC spectra and the $\nu_M(T)$ trends of the other $RCo_2$ are given in Ref. 3. The data in Fig. 2 show clearly that it is quite easy for PAC (and the same holds for other HFI techniques) to discriminate between first and second-order transitions: While the magnetic hyperfine frequency of $^{111}$Cd in $GdCo_2$ decreases continuously towards the phase transition, $\nu_M(T)$ of $PrCo_2$ and $HoCo_2$ varies little with temperature and collapses discontinuously from a value close to saturation to zero within an experimental temperature interval of $(1-T/T_{C0})\sim 5\times 10^{-3}$.

The magnetic hyperfine field $B_{hf}$ at a probe nucleus and the magnetization $M$ of the ferromagnetic host are related by the hyperfine coupling constant.[11] As a rule, the coupling constant *decreases* with increasing temperature, i.e., the hyperfine field decreases faster with temperature than the host magnetization. The extent of the decrease depends on the electronic properties of the probe atom: For solutes with a localized magnetic moment, the magnetic hyperfine field may decrease much faster than the host magnetization. As examples we cite the NMR study of $^{55}$Mn in Fe by Koi *et al.*[12] and the PAC study of $^{99}$Ru in Ni by Shirley *et al.* [13] For closed-shell probe atoms without a localized moment such as $^{111}$Cd or $^{119}$Sn, the hyperfine field usually decreases slightly faster than the host magnetization. This holds for the elemental ferromagnets [see, e.g., $^{111}$Cd in Ni (Refs. 13 and 14) or $^{111}$Cd in Gd (Ref. 15)] as well as for magnetically ordered intermetallic compounds [see, e.g., $^{119}$Sn in $GdAl_2$ (Ref. 16), $^{119}$Sn in $Gd_2In$ (Ref. 17) or $^{111}$Cd in $R_2In$ (Ref. 18)].

In order to reconcile an almost temperature independent magnetic hyperfine field showing a discontinuous collapse at $T_C$ with the second-order transition of the host magnetization proposed by Herrero-Albillos *et al.*[1,2] for $PrCo_2$ and $NdCo_2$, one would have to postulate a *critical increase* of the hyperfine coupling constant towards the phase transition. There is, however, no support for such an anomaly of the hyperfine coupling constant of $^{111}$Cd in $RCo_2$, neither from experimental data nor from theoretical considerations. In all $RCo_2$ compounds with SOT's ($GdCo_2$, $TbCo_2$, $SmCo_2$) and also in those with unquestioned FOT's ($ErCo_2$, $HoCo_2$, and $DyCo_2$) the temperature dependence of the $^{111}$Cd hyperfine field follows closely that of the host magnetization[3] and one has no reasonable argument to assume that only $PrCo_2$ and $NdCo_2$ differ in this aspect. Hence, it is difficult to avoid the conclusion that in $PrCo_2$ and $NdCo_2$ the spontaneous magnetization undergoes a discontinuous, first-order transition from the ferromagnetic to the paramagnetic state.

This conclusion is not affected by the observation of a distribution of the order temperatures in the investigated compounds. Evidence for a spread of the Curie temperatures of a few degrees Kelvin comes (i) from the critical increase of the relative linewidth of the magnetic hyperfine field and (ii) from the coexistence of the paramagnetic and the ferromagnetic phase in a small temperature interval near $T_{C0}$ both in SOT and FOT compounds. For details and illustration see Figs. 2 and 9 in Ref. 3. Critical increase of the linewidth and phase coexistence are no singularities of $RCo_2$. Such indications of a $T_C$ distribution have been observed in practically all hyperfine field studies of chemically ordered magnetic compounds reported up to now.[16,18–20]

This high sensitivity to inhomogeneities of the magnetic properties of a given sample is one of the outstanding qualities of hyperfine spectroscopic techniques. The fact that hyperfine interactions—both magnetic and electric—are very short-ranged results in a nanometer spatial resolution and enables PAC, Mössbauer, NMR and other HFI techniques to identify different local configurations in the same sample. Consequently, these microscopic methods are sensitive to local variations of the exchange interaction and the order temperature. This quality is unmatched by macroscopic techniques such as magnetization, resistivity or DSC measurements which observe average quantities and therefore may have difficulties in perceiving magnetic inhomogeneities resulting, e.g., from a distribution of the order temperature.

Contrary to what Herrero-Albillos *et al.*[1,2] suggest, critical increase of the linewidth and phase coexistence pose no problem for the identification of a FOT. The contributions of the paramagnetic and the ferromagnetic phase to the PAC spectrum at a given temperature are easily separated because the two phases have completely different perturbation factors. The absence of an interaction in the paramagnetic phase results in a time-independent anisotropy while the ferromagnetic phase is characterized by a periodic modulation of the anisotropy. As a consequence, the thermal evolution of the paramagnetic phase upon heating across the phase transition can be followed quantitatively and the magnetic interaction remains visible to the last magnetically ordered grain of the sample.

The increase of the linewidth is severe when the magnetic

interaction frequency varies strongly with the Curie temperature. This is the case for SOT's rather than FOT's. For SOT's the frequency varies critically as $\nu_M(T) \propto (1-T/T_C)^{\beta}$ with an exponent $\beta \sim 0.3-04$ (Ref. 4), whereas for FOT's $\nu_M(T)$ changes only slightly. In Ref. 3 it has been shown in great detail that in spite of the increase of the linewidth, the temperature dependence of the magnetic frequency can be precisely measured down to $\nu_M(T) \geqslant 0.1-0.2\ \nu_M(0)$. Due to this lower frequency limit it may be difficult to distinguish a FOT with a small discontinuity of the order parameter ($\leqslant 20\%$ of the saturation value) from a SOT. In the case of $PrCo_2$ and $NdCo_2$, however, one has $\nu_M(T_{C0}) \sim 0.9\nu_M(0)$ and $\nu_M(T_{C0}) \sim 0.55\nu_M(0)$, respectively, far above the lower frequency limit. The hyperfine interaction data of $^{111}$Cd in $PrCo_2$ and $NdCo_2$ are therefore incompatible with a SOT of the magnetization of these compounds.

It might be that for perfect solids, "DSC is the technique of choice when aiming at determine the nature of a transition." The data of Herrero-Albillos *et al.*,[1,2] however, convey the impression that in real-physics materials it is not as easy and unambiguous for DSC to distinguish between a SOT and a FOT as suggested by these authors. The conclusion of SOT's for $PrCo_2$ and $NdCo_2$ is based on the λ-shaped zero-field DSC curve, the broadening of the peak when a field is applied, the fact that the peak does not shift with increasing field and the absence of thermal and field hysteresis. Very similar observations, however, have been made for the FOT compound $DyCo_2$. The zero-field DSC curve of this compound shows a wide peak with a width of the order of 5 K which resembles much more the DSC curves of $PrCo_2$ and $NdCo_2$ than that of the FOT compound $ErCo_2$ and the thermal or field hysteresis expected for FOT's was absent in the sample of $DyCo_2$ described in Ref. 1.

To reconcile these DSC data of $DyCo_2$ with the unquestioned FOT character of the compound, Herrero-Albillos *et al.*[1,2] propose a "weak" FOT for $DyCo_2$ without discussing how the magnitude of the order parameter at $T_C$ affects hysteresis and shape of the DSC curve. The PAC results[3] clearly show that the FOT of $DyCo_2$ is not much "weaker" than that of $HoCo_2$: the discontinuity of the order parameter at $T_C$ of $DyCo_2$ is only slightly smaller than in $HoCo_2$. The DSC curves—with and without field—of the two compounds, however, differ substantially, which suggests that the DSC data suffer from the influence of factors yet to be identified.

Magnetic disorder might be among these factors. In spite of the strong PAC evidence for $T_C$ distributions in $RCo_2$, the question to which extent magnetic imperfections may obfuscate the DSC conclusions on the order of the phase transitions has not been addressed by Herrero-Albillos *et al.*[1,2] The authors have characterized their samples by x-ray diffraction measurements, but—contrary to the HFI techniques—these provide no information on slight magnetic disorder. As DSC measurements integrate over the entire sample, the effect of, e.g., a spread of the order temperature on the DSC curve will depend on the details of the $T_C$ distribution. In cases where a FOT sample contains two discrete components with slightly different stoichiometry, each one with its own sharp order temperature, one would expect two discrete peaks in the DSC curve. Depending on the difference of the order temperatures, such a situation can be resolved by DSC, as shown by the $HoCo_2$ data. In the case of continuous $T_C$ distributions with a width of a few K, as they are evidenced by the PAC measurements, the DSC curve of a FOT compound would be altered by the shape of this distribution and could probably take any form, ranging from λ shape to a broad peak. The observation of a sharp DSC peak in one FOT compound ($ErCo_2$) is no argument for the absence of a $T_C$ distribution in other FOT substances.

It might also be important that PAC and DSC measurements sample different aspects of the $RCo_2$ magnetization. The dominant contribution to the $^{111}$Cd hyperfine field comes from the *s*-electron spin polarization induced by the polarized 3*d* band and is therefore roughly proportional to the Co moment which changes only slightly between the light and the heavy $RCo_2$. On the other hand, as pointed out by de Oliveira *et al.*,[21] the jump observed in the magnetic entropy curve around $T_C$ is due to the coupling between the localized 4*f* spins and the magnetic moment induced at the Co sites. In the light rare earth the 4*f* electrons are less well localized and therefore more susceptible to crystal field interactions which may affect the 4*f*-3*d* coupling. This raises the question of the order of magnitude to be expected for the entropy jump at FOT's of light $RCo_2$ and how it compares to the experimental DSC accuracy.

In summary, the assessment of our PAC study[3] of $RCo_2$ by Herrero-Albillos *et al.*[1,2] is unsubstantiated and does not resolve the conflict between the conclusions drawn from the PAC and the DSC data on the order of the phase transitions of $PrCo_2$ and $NdCo_2$. PAC and other microscopic techniques not only allow a qualitative distinction between FOT's and SOT's, but also a precise quantitative determination of the order parameter at the transition, as recently illustrated by a $^{111}$Cd PAC study[22] of the $T_C$ dependence of $\nu_M(T_C)/\nu_M(0)$ in $R_{1-x}Y_xCo_2$. Moreover—and probably important in the present context—hyperfine spectroscopic techniques are able to provide quantitative information on magnetic imperfections which are not accessible to macroscopic techniques such as DSC. The PAC data leave no choice to the conclusion that in $PrCo_2$ and $NdCo_2$ the spontaneous magnetization undergoes a discontinuous, first-order phase transition at $T_C$.

The analysis of the temperature dependence of the $YCo_2$ band structure by Bloch *et al.*[7] led to the conclusion that the fourth-order term of the Landau free energy of $RCo_2$ becomes negative at $T < T_0$ ($T_0 \sim 200$ K, Ref. 22). The Landau theory[8] then predicts that at $T_C < T_0$ the phase transitions change from second to first order. Prior to our measurements this concept was believed to apply only to the heavy $RCo_2$. Our experimental results for $PrCo_2$ and $NdCo_2$, however, show that the Bloch-Shimizu theory consistently describes the order of the phase transitions both in heavy and light $RCo_2$.

*Corresponding author; electronic address: forker@iskp.uni-bonn.de

†Present address: Instituto de Magnetismo Aplicado, PO Box 155, 28230 Las Rozas, Madrid, Spain.

[1] J. Herrero-Albillos, F. Bartolomé, L. M. Garcia, F. Casanova, A. Labarta, and X. Batlle, Phys. Rev. B **73**, 134410 (2006).

[2] J. Herrero-Albillos, F. Casanova, F. Bartolomé, L. M. García, A. Labarta, and X. Batlle, J. Magn. Magn. Mater. **290-291**, 682 (2005).

[3] M. Forker, S. Müller, P. de la Presa, and A. F. Pasquevich, Phys. Rev. B **68**, 014409 (2003).

[4] C. Hohenemser, N. Rosov, and A. Kleinhammes, Hyperfine Interact. **49**, 267 (1989).

[5] E. Gratz and A. S. Markosyan, J. Phys.: Condens. Matter **13**, R385 (2001).

[6] N. H. Duc and P. E. Brommer, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amterdam, 1999), Vol. 12, p. 259.

[7] D. Bloch, M. Edwards, M. Shimizu, and J. Voiron, J. Phys. F: Met. Phys. **5**, 1217 (1975).

[8] M. Shimizu, Rep. Prog. Phys. **44**, 329 (1981).

[9] P. de la Presa, S. Müller, A. F. Pasquevich, and M. Forker, J. Phys.: Condens. Matter **12**, 3423 (2000).

[10] H. Frauenfelder and R. M. Steffen, in *Perturbed Angular Correlations*, edited by K. Karlsson, E. Matthias, and K. Siegbahn (North-Holland, Amsterdam, 1963).

[11] E. P. Wohlfarth, in *Ferromagnetic Materials*, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1980), Vol. 1, Chap. 1.

[12] Y. Koi, A. Tsujimura, and T. Hihara, J. Phys. Soc. Jpn. **19**, 1493 (1964).

[13] D. A. Shirley, S. S. Rosenblum, and E. Matthias, Phys. Rev. **170**, 363 (1968).

[14] B. Lindgren and Y. K. Vijay, Hyperfine Interact. **9**, 379 (1982).

[15] L. Boström, G. Liljegren, B. Jonsson, and E. Karlsson, Phys. Scr. **3**, 175 (1971).

[16] N. N. Delyagin, V. I. Nesterov, and S. I. Reiman, Sov. Phys. JETP **57**, 922 (1983).

[17] N. N. Delyagin, G. T. Muzhiri, V. I. Nesterov, and S. I. Reiman, Sov. Phys. JETP **59**, 592 (1984).

[18] M. Forker, R. Müsseler, S. C. Bedi, M. Olzon-Dionysio, and S. D. de Souza, Phys. Rev. B **71**, 094404 (2005).

[19] B. A. Komissarova, G. K. Ry, I. G. Shnipkova, A. A. Sorokin, A. V. Tavyaschenko, L. M. Fomichova, and A. S. Denisova, Aust. J. Phys. **51**, 175 (1998).

[20] A. T. Motta, G. L. Catchen, S. E. Cumblidge, R. L. Rasera, A. Paesano, and L. Amaral, Phys. Rev. B **60**, 1188 (1999).

[21] N. A. de Oliveira, P. J. von Ranke, M. V. Tovar Costa, and A. Troper, Phys. Rev. B **66**, 094402 (2002).

[22] M. Forker, P. de la Presa, and A. F. Pasquevich, J. Phys.: Condens. Matter **18**, 253 (2006).